

WHAT IS CLAIMED IS:

- 1                    1.     A method for removing and recovering an ion from a solution  
2 comprising:  
3                    (a)     contacting said solution with a solid ion extractant comprising a  
4 recyclable activated ion coordinating agent to remove at least a portion of said ion from said  
5 solution;  
6                    (b)     deactivating said ion coordinating agent;  
7                    (c)     dissolving said ion in a recovery solvent and removing said ion from  
8 said solid ion extractant; and  
9                    (d)     recovering said ion from said recovery solvent.
- 1                    2.     The method of Claim 1, wherein said ion is an anion.
- 1                    3.     The method of Claim 1, wherein said ion is a perfluoroalkylsulfonate  
2 or a perfluoroalkyl carboxylate.
- 1                    4.     The method of Claim 1, wherein said ion coordinating agent comprises  
2 a lipophilic portion.
- 1                    5.     The method of Claim 1, wherein said active ion coordinating agent is  
2 ionizable in an aqueous solution.
- 1                    6.     The method of Claim 1, wherein said step of removing said ion from  
2 said solution comprises an ion-exchange process.
- 1                    7.     The method of Claim 1, wherein said ion coordinating agent is an  
2 organometallic compound.
- 1                    8.     The method of Claim 7, wherein said ion coordinating agent is redox-  
2 recyclable.
- 1                    9.     The method of Claim 8, wherein said ion coordinating agent is  
2 oxidized prior to said step (a).
- 1                    10.    The method of Claim 9, wherein said oxidation step comprises an  
2 electrochemical oxidation process.

11. The method of Claim 9, wherein said oxidation step comprises a chemical oxidation process.

12. The method of Claim 8, wherein said deactivation step comprises reducing said ion coordinating agent.

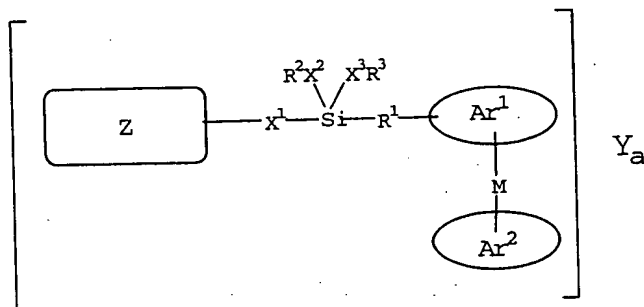
13. The method of Claim 12, wherein said reduction step comprises an electrochemical reduction process.

14. The method of Claim 12, wherein said reduction step comprises a chemical reduction process.

15. The method of Claim 14, wherein said chemical reduction process comprises contacting said solid ion extractant with a deactivating solution.

16. The method of Claim 15, wherein said deactivating solution comprises a compound selected from the group consisting of  $\text{Na}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{Cr}^{2+}$  salt,  $\text{V}^{2+}$  salt and  $\text{NaBH}_4$ .

17. The method of Claim 1, wherein said solid ion extractant is a composition of the formula:



wherein

each of  $\text{Ar}^1$  and  $\text{Ar}^2$  is independently  $\text{C}_4\text{-C}_{20}$  aryl;

$\text{M}$  is a transition metal;

$\text{R}^1$  is  $\text{C}_2\text{-C}_{20}$  alkylene;

each of  $\text{X}^1$ ,  $\text{X}^2$  and  $\text{X}^3$  is independently a bond,  $\text{O}$ ,  $\text{S}$ , or  $\text{NR}^4$ ;

each of  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  is independently  $\text{H}$ , or  $\text{C}_1\text{-C}_6$  alkyl;

$\text{Z}$  is a solid support;

$\text{Y}$  is an anion; and

12 a is 0 when said ion coordinating agent is deactivated, and  
13 a is an integer from 1 to 3 when said ion coordinating agent is activated.

1 18. The method of Claim 17, wherein M is selected from the group  
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 19. The method of Claim 17, wherein Ar<sup>1</sup> and Ar<sup>2</sup> are selected from the  
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be  
3 optionally substituted.

1 20. The method of Claim 17, wherein each of X<sup>1</sup>, X<sup>2</sup> and X<sup>3</sup> is  
2 independently a bond or O.

1 21. The method of Claim 17, wherein R<sup>2</sup> and R<sup>3</sup> are C<sub>1</sub>-C<sub>6</sub> alkyl.

1 22. The method of Claim 17, wherein said solid support is glass or a  
2 polymeric resin.

1 23. The method of Claim 22, wherein said polymeric resin is selected from  
2 the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and  
3 polyaromatic.

1 24. The method of Claim 17, wherein Y is selected from the group  
2 consisting of nitrate, halide, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, carboxylate and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>.

1 25. The method of Claim 17, wherein a is 1 when said ion coordinating  
2 agent is activated.

1 26. The method of Claim 1, wherein said solution is an aqueous solution.

1 27. The method of Claim 26, wherein the temperature of solution of said  
2 step (a) is least about 24 °C.

1 28. The method of Claim 1, wherein the temperature of said recovery  
2 solution is at least about 85 °C.

29. The method of Claim 28, wherein said recovery step (d) comprises reducing the temperature of said recovery solution to less than about 5 °C to precipitate said ion.

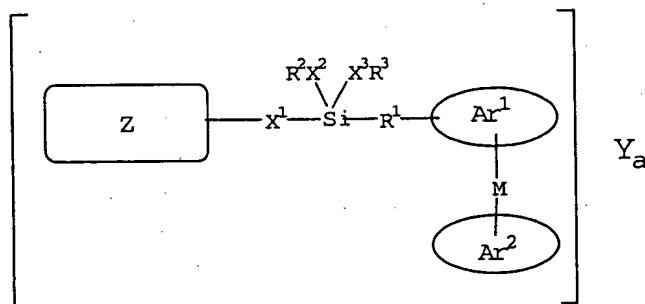
30. The method of Claim 29, wherein said recovery step further comprises separating said precipitated ion from said recovery solution.

31. The method of Claim 1, further comprising:

- (e) re-activating said deactivated ion coordinating agent; and
- (f) repeating said steps (a)-(e).

32. A method for removing and recovering an anion from an aqueous solution comprising:

- (a) contacting said solution with a solid ion extractant comprising an ion coordinating agent to remove at least a portion of said anion from said aqueous solution, wherein said solid ion extractant is a composition of the formula:



wherein

each of Ar<sup>1</sup> and Ar<sup>2</sup> is independently C<sub>4</sub>-C<sub>20</sub> aryl;

M is a transition metal;

R<sup>1</sup> is C<sub>2</sub>-C<sub>20</sub> alkylene;

each of X<sup>1</sup>, X<sup>2</sup> and X<sup>3</sup> is independently a bond, O, S, or NR<sup>4</sup>;

each of R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is independently H, or C<sub>1</sub>-C<sub>6</sub> alkyl;

Z is a solid support;

Y is an anion; and

a is an integer from 1 to 3;

- (b) reducing said ion coordinating agent in said solid ion extractant such

that a is 0;

- 18 (c) dissolving said anion in a recovery solvent and removing said anion  
19 from said solid ion extractant; and  
20 (d) recovering said anion.

1 33. The method of Claim 32, wherein said anion is a perfluoroalkyl  
2 sulfonate or perfluoroalkyl carboxylate.

1 34. The method of Claim 32, wherein said step of removing said anion  
2 from said aqueous solution comprises an ion-exchange process.

1 35. The method of Claim 32, wherein a in said step (a) is 1.

1 36. The method of Claim 32, wherein said ion coordinating agent is redox-  
2 recyclable.

1 37. The method of Claim 36, further comprising a step of oxidizing said  
2 ion coordinating agent from  $a=0$  to  $a=1$  prior to said step (a).

1 38. The method of Claim 37, wherein said oxidizing step comprises an  
2 electrochemical oxidation process.

1 39. The method of Claim 37, wherein said oxidizing step comprises a  
2 chemical oxidation process.

1 40. The method of Claim 36, wherein said deactivation step comprises  
2 reducing said ion coordinating agent.

1 41. The method of Claim 40, wherein said reducing step comprises an  
2 electrochemical reduction process.

1 42. The method of Claim 40, wherein said reducing step comprises a  
2 chemical reduction process.

1 43. The method of Claim 42, wherein said chemical reduction process  
2 comprises contacting said solid ion extractant with a deactivating solution.

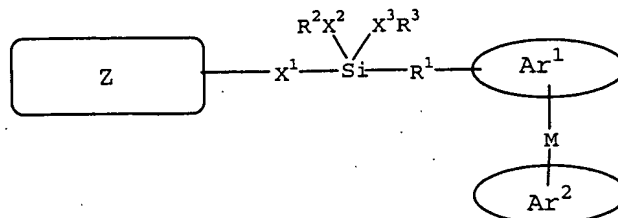
1 44. The method of Claim 43, wherein said deactivating solution comprises  
2 a compound selected from the group consisting of  $\text{Na}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{Cr}^{2+}$   
3 salt,  $\text{V}^{2+}$  salt and  $\text{NaBH}_4$ .

- 1                    45.    The method of Claim 32, wherein M is selected from the group  
2    consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.
- 1                    46.    The method of Claim 45, wherein Ar<sup>1</sup> and Ar<sup>2</sup> are selected from the  
2    group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be  
3    optionally substituted.
- 1                    47.    The method of Claim 46, wherein each of X<sup>1</sup>, X<sup>2</sup> and X<sup>3</sup> is  
2    independently a bond or O.
- 1                    48.    The method of Claim 47, wherein R<sup>2</sup> and R<sup>3</sup> are C<sub>1</sub>-C<sub>6</sub> alkyl.
- 1                    49.    The method of Claim 48, wherein said solid support is glass or a  
2    polymeric resin.
- 1                    50.    The method of Claim 49, wherein said polymeric resin is selected from  
2    the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and  
3    polyaromatic.
- 1                    51.    The method of Claim 50, wherein Y is selected from the group  
2    consisting of nitrate, halide, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, carboxylate and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>.
- 1                    52.    The method of Claim 32, wherein the temperature of said aqueous  
2    solution of said step (a) is least about 24 °C.
- 1                    53.    The method of Claim 52, wherein the temperature of said recovery  
2    solution is at least about 85 °C.
- 1                    54.    The method of Claim 53, wherein said recovery step (d) comprises  
2    reducing the temperature of said recovery solution to less than about 5 °C to precipitate said  
3    anion.
- 1                    55.    The method of Claim 54, wherein said recovery step further comprises  
2    separating said precipitated ion from said recovery solution.
- 1                    56.    The method of Claim 32, further comprising:  
2    (e)    re-activating said deactivated ion coordinating agent; and

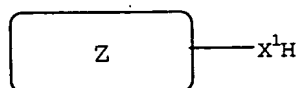
(f) repeating said steps (a)-(e).

57. A process for producing a solid ion extractant composition of the

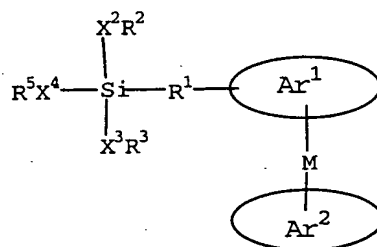
formula:



said process comprising contacting the solid support of the composition:



with an ion coordinating agent of the formula:



wherein

each of Ar<sup>1</sup> and Ar<sup>2</sup> is independently C<sub>4</sub>-C<sub>20</sub> aryl;

each of X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> and X<sup>4</sup> is independently a bond, O, S, or NR<sup>4</sup>;

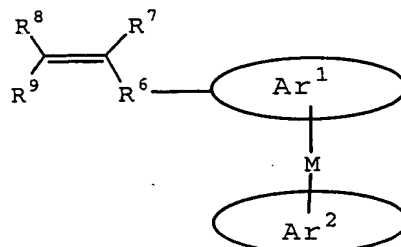
R<sup>1</sup> is C<sub>2</sub>-C<sub>20</sub> alkylene;

each of R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> is independently H, or C<sub>1</sub>-C<sub>6</sub> alkyl;

M is a transition metal; and

Z is a solid support.

58. The process of Claim 57, further comprising the step of producing said ion coordinating agent, wherein said ion coordinating agent producing step comprises contacting an olefin of the formula:



5 with a silyl compound of the formula  $\text{HSi}(\text{X}^2\text{R}^2)(\text{X}^3\text{R}^3)(\text{X}^4\text{R}^5)$  in the presence of a catalyst to  
6 produce said ion coordinating agent,  
7 wherein

8  $\text{R}^6$  is a bond or  $\text{C}_1\text{-C}_{18}$  alkylene; and  
9 each of  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  is independently H or  $\text{C}_1\text{-C}_6$  alkyl.

1 59. The method of Claim 58, wherein said catalyst is selected from the  
2 group consisting of Karstedt's catalyst, Speier's catalyst, other silylplatinum complexes,  
3 transition metal nanoclusters, dicobalt octacarbonyl, nickel tetracarbonyl, Wilkinson's  
4 catalyst, chromium hexacarbonyl, and zirconocenes.

1 60. The process of Claim 57, wherein M is selected from the group  
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 61. The process of Claim 60, wherein  $\text{Ar}^1$  and  $\text{Ar}^2$  are selected from the  
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be  
3 optionally substituted.

1 62. The process of Claim 61, wherein each of  $\text{X}^1$ ,  $\text{X}^2$  and  $\text{X}^3$  are  
2 independently a bond or O.

1 63. The process of Claim 62, wherein  $\text{X}^4$  is O.

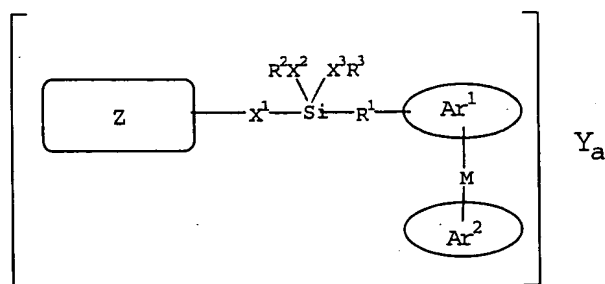
1 64. The process of Claim 63, wherein  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^5$  are  $\text{C}_1\text{-C}_6$  alkyl.

1 65. The process of Claim 64, wherein said solid support is glass or a  
2 polymeric resin.

1 66. The process of Claim 65, wherein said polymeric resin is selected from  
2 the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and  
3 polyaromatic.

1 67. The process of Claim 57, further comprising oxidizing said solid ion  
2 extractant to produce an activated solid ion extractant of the formula:





wherein

Y is an anion; and

a is an integer from 1 to 3.

68. The process of Claim 67, wherein a is 1.

69. The process of Claim 67, wherein Y is selected from the group consisting of nitrate, halide,  $\text{HSO}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{ReO}_4^-$ ,  $\text{PF}_6^-$ , carboxylate and  $\text{CF}_3\text{SO}_3^-$ .

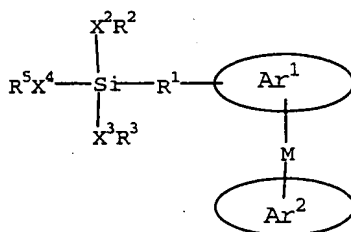
70. The process of Claim 67, wherein said oxidizing step comprises an electrochemical oxidation process.

71. The process of Claim 67, wherein said oxidizing step comprises a chemical oxidation process.

72. The process of Claim 71, wherein said chemical oxidation process comprises contacting said solid ion extractant with a solution comprising an oxidant to produce said activated solid ion extractant.

73. The process of Claim 72, wherein said oxidant is selected from the group consisting of  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{AgNO}_3$ ,  $\text{FeCl}_3$ ,  $\text{AgF}$ ,  $\text{NaOCl}$ ,  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  and  $\text{Ce}(\text{SO}_4)_2$ .

74. A compound of the formula:



wherein

each of  $\text{Ar}^1$  and  $\text{Ar}^2$  is independently  $\text{C}_4\text{-C}_{20}$  aryl;

each of  $\text{X}^1$ ,  $\text{X}^2$ ,  $\text{X}^3$  and  $\text{X}^4$  is independently a bond, O, S, or  $\text{NR}^4$ ;

6           R<sup>1</sup> is C<sub>2</sub>-C<sub>20</sub> alkylene;  
7           each of R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> is independently H, or C<sub>1</sub>-C<sub>6</sub> alkyl; and  
8           M is a transition metal.

1           75.    The compound of Claim 74, wherein M is selected from the group  
2   consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1           76.    The compound of Claim 74, wherein Ar<sup>1</sup> and Ar<sup>2</sup> are selected from the  
2   group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be  
3   optionally substituted.

1           77.    The compound of Claim 74, wherein each of X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> and X<sup>4</sup> is  
2   independently a bond or O.

1           78.    The compound of Claim 74, wherein R<sup>2</sup> and R<sup>3</sup> are C<sub>1</sub>-C<sub>6</sub> alkyl.